GROWING NANOWIRES

Tiny semiconducting strings for virtually every purpose

"THERE IS THIS REMARKABLE HISTORY in which the semiconductor components of computer chips have gotten smaller each year, with performance improving along with the miniaturization," says Jennifer Hollingsworth, a Los Alamos materials chemist specializing in nanotechnology. Hollingsworth constructs quantum dots and nanowires, the ultimate in miniature semiconductors, with potential uses that reach far beyond computer chips. "But we're going about it from the opposite direction: building tiny semiconducting structures from the bottom up."

Hollingsworth is the co-science leader of the nanowire integration focus area within the Center for Integrated Nanotechnologies (CINT), a joint enterprise between Los Alamos and Sandia national laboratories in New Mexico. Like four other Nanoscale Science Research Centers, CINT is a premier Department of Energy (DOE) user facility for interdisciplinary research that serves as the basis for a national nanoscience initiative, encompassing new science, new tools, and new computing capabilities.

That's where Hollingsworth and her nanoscale semiconductors fit in. Renowned for finding a solution to a long-standing "blinking" problem with quantum dots (switching off and on), she has recently turned her attention to novel semiconductor nanowires and new methods for growing them. She invented a method that would enable unprecedented control over nanowire fabrication in solution, promising lower cost and lower-temperature growth and processing. At the same time, the wires would be of high quality with structures designed to suit particular applications—important attributes for making commercially viable nanowire components.

"At that point," Hollingsworth says, "a lot of technological progress will follow." Indeed, semiconductor nanowires are expected to bring about transformative improvements to solar cells, rechargeable batteries, thermoelectric energy converters, biomedical devices, computers, sensors, and a host of other electronics.

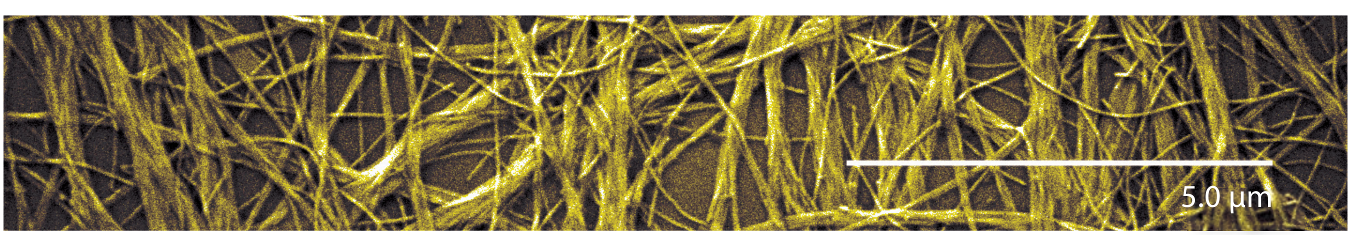
What's in a wire?

Quantum dots and nanowires owe their special properties partly to the semiconductor materials they are made from and partly to their miniscule size. The properties of semiconductors—whether in bulk, miniaturized, or nanoscale—are derived from their internal energy structure: Most of their electrons possess energies within a particular range known as the valence band, while a few are in a higher-energy range known as the conduction band, with an unoccupied energy gap in between. In general, the greater the number of valence-band electrons that can be manipulated into jumping the energy gap to the conduction band, the more electrical current the material will support.

In one of a computer chip's many transistors, for example, a voltage can be temporarily applied to supply the energy needed to populate a semiconductor's conduction band in such a way as to create a new conducting path. This essentially has the effect of flipping a switch, but with no moving parts, so it allows the computer to rearrange its own circuitry to perform different calculations and execute a variety of programs. Outside of computing, semiconductivity is also the basis of many other important technologies, including LED-based lights and lasers, solar cells, and a number of ubiquitous circuit components.

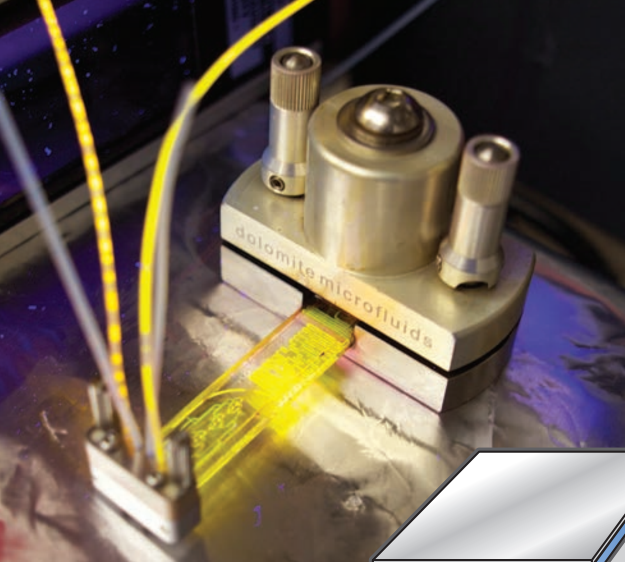
In terms of size, nanoparticles (dots or wires) are often just nanometers (10^{-9} meter) in diameter, less than one-ten-thousandth the diameter of a human hair. At that small size, electrons experience something called quantum confinement, in which the physics that governs their behavior is altered because they are "squeezed" by their confined space. The effect adjusts the structure of the semiconductor's energy bands and the gap between: the smaller the nanoparticle, the greater the energy gap. Therefore a desired energy gap can be obtained simply by constructing a nanoparticle of the correct size. Furthermore, because a larger-than-usual fraction of the atoms or molecules in a nanoparticle reside on its exterior surface, their quantum "surface physics" comes into play much more than it would in a larger object. Among other things, this makes quantum dots and nanowires extremely sensitive to the presence of small entities nearby, making them useful for detecting particular molecules in chemical and biological applications.

Taken together, semiconductivity and quantum confinement allow scientists and engineers to meet an incredible variety of technological challenges. Want a faster microprocessor? Cram an enormous number of tiny nanowire-based transistors onto your chip. Want a solar cell that draws more energy from sunlight? Arrange your nanowires to maximize



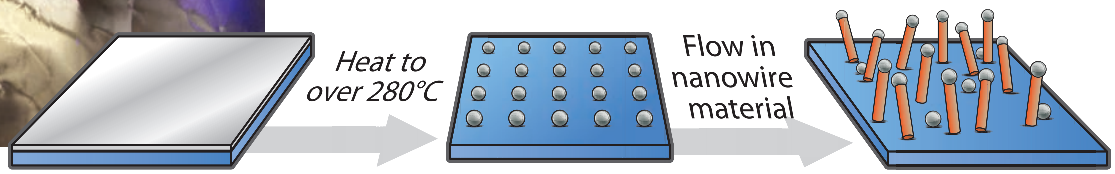
Electron micrograph images of nanowires in the "spaghetti" and "forest" configurations. (Above) These cadmium selenide nanowire strands and "ropes" were grown in the solution phase and deposited on a solid substrate, or surface. (Opposite page) This false-color electron micrograph shows gallium nitride nanowires on a silicon substrate, designed to emit visible and ultraviolet light for laser applications and other uses.

CREDIT: (above) Jennifer Hollingsworth's lab/LANL; (opposite) Lorelle Mansfield/NIST



(Left) The flow-SLS device (yellow), with fluid inlet and outlet tubes (also yellow), is set inside a stainless-steel mounting (center) that preheats incoming fluid and maintains a constant temperature throughout the growth region inside. (Below) The Los Alamos microfluidic flow-SLS nanowire growth method, like the more common vapor-phase method, starts with a substrate in a reaction chamber. The substrate (blue) is coated with a thin bismuth film (white); upon heating, the film breaks into small droplets which will catalyze the nanowire growth. When the nanowire material is flowed into the reactor via a carrier solvent (along with some necessary additives), it enters the catalyst droplets and subsequently crystallizes onto the interface between the droplets and the substrate below, thereby growing the nanowires from the bottom up.

CREDIT: Jennifer Hollingsworth/LANL



light absorption and minimize reflection. Want to detect an individual protein molecule associated with cancer? Design the energy levels of a nanowire device to populate its conduction band in response to electrical charges on the protein's binding surface. The possibilities truly abound—if controlled nanoparticle synthesis can be made cost effective at the industrial scale.

Tale of two syntheses

Semiconductor nanowires may prove more versatile than quantum dots for some applications. Whereas quantum dots are nano-sized in all three dimensions, nanowires are nano-sized in only two. They have one long dimension, typically 20 to 1000 times longer than the wire's diameter. And because of their long dimension, they can be manipulated, anchored on the ends, and arranged in different configurations to suit the needs of different applications. When used in solar cells, for instance, nanowires offer a significant advantage over quantum dots. The wire shape is better for conveying photoelectrons (individual units of solar electricity) into whatever external circuit the solar cell is connected to before they disappear by ineffectually recombining with the electrical charge "holes" left behind during their production.

There are two primary methods for making nanowires, each with its pros and cons. Unlike most other nanotech facilities, Hollingsworth points out, CINT does both.

One method, called vapor-liquid-solid synthesis, or vapor-phase synthesis, starts with tiny nanocluster droplets of a liquid metal catalyst, such as liquid gold, arranged on a substrate (surface). A semiconducting material such as silicon, from which the nanowire will be made, is then injected in vapor form into the chamber housing the substrate. The vapor diffuses into the liquid metal droplets until it supersaturates, at which point it crystallizes onto the substrate at the base of the droplet. As the process continues, each newly deposited bit of crystal builds upon the last, causing a nanowire to grow vertically, elevating the catalyst droplet as it grows. When a "forest" of nanowires (so named because they stand parallel to one another like trees) grows to the desired nanowire height, the vapor inflow is shut off.

Jinkyoung Yoo is a colleague of Hollingsworth's at CINT who specializes in growing nanowires by vapor-phase synthesis. This method allows him to produce extremely high-quality nanowires—pure of composition and defect-free—in the forest arrangement that's favored for use in solar collectors and electronic devices. The vapor-phase method also permits him to make the wires "heterostructured"—alternating between two opposing types of semiconducting materials—by flowing the vapors of each material into the chamber in an alternating sequence. This, too, is important for electronics applications, which require joining the two types of semiconductors, *p*-type and *n*-type, to make what's called a *p-n* junction. (The letters indicate positive and negative, referring to their tendency to either accept or donate electrons. At a *p-n* junction, the *n*-type semiconductor donates electrons to the *p*-type semiconductor.)

"With vapor-phase growth, you can make *p-n* junctions in individual heterostructured nanowires," says Yoo, "and you can make more complex logical elements like transistors by crossing those wires." Indeed, vapor-phase is the method of choice for anyone wanting enough control over the growth process to produce forest-style, heterostructured nanowires for electronic devices. But the process is slow, and it's expensive due to the high-purity semiconductor starting materials needed. Those starting materials are both toxic and flammable, adding to the expense with the required safety precautions. For these reasons, although vapor-phase has already proven its value at the laboratory scale and in industry R&D—permitting fine-tuning of composition, conductivity, energy band spacing, and so on—it may prove impractical at the production scale, when expense becomes the driving factor.

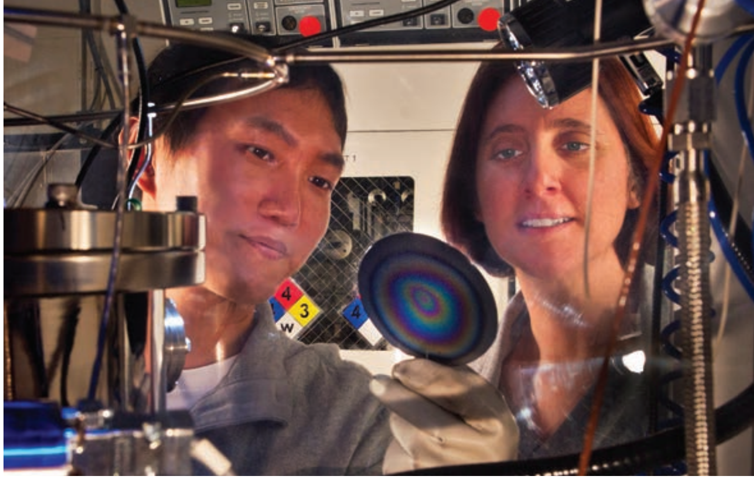
The other common method, called solution-liquid-solid synthesis, is a type of solution-based synthesis that's less expensive and scales up easily. The nanowires can be grown in large batches in solution. Like vapor-liquid-solid growth, molten metal nanocrystals are used as a growth catalyst. Here, however, they are immersed in a solvent, so that when semiconductor precursor chemicals are released into the solution, they become incorporated into the liquid metal particles until the semiconductor nucleates and grows into a nanowire structure. The solution-based growth process is about a thousand times faster than vapor-phase synthesis, taking as little as seconds or minutes to complete. Once finished, the nanowires have the additional benefit that, because they're soluble, they can be sprayed, dip-coated, or painted onto a surface. For certain applications, this flexibility, in addition to the potentially large batch sizes, equates to low cost.

But of course there's a catch. With the speed and relative ease of growth in solution comes a loss in quality and control. Solution-based synthesis takes place at a lower temperature than vapor-phase synthesis, and that lower temperature can lead to structural defects. Also, instead of slow, consistent growth with a measured and controlled rate of precursor incorporation and removal of byproducts, the concentration of reactants varies throughout the process, with no removal of byproducts. Finally, because the solution method is essentially an all-at-once process, it's impractical to make heterostructured nanowires. So solution-based synthesis scales up to industrial use well, but lacks the precision of the vapor-phase method to create the high-quality, forest-style, heterostructured nanowires required for many applications.

If only there were a way to combine the two.

Best of both worlds

"We needed a way to achieve the controllability of the vapor-flow method while maintaining some of the practical, ease-of-use benefits and lower cost of solution chemistry," Hollingsworth explains. "In other words, we needed a flow-based solution process that's slow and steady enough to adjust and optimize, with the potential to scale up." The resulting innovation? Flow-based solution-liquid-solid synthesis, or flow-SLS for short.

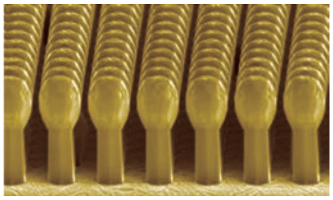


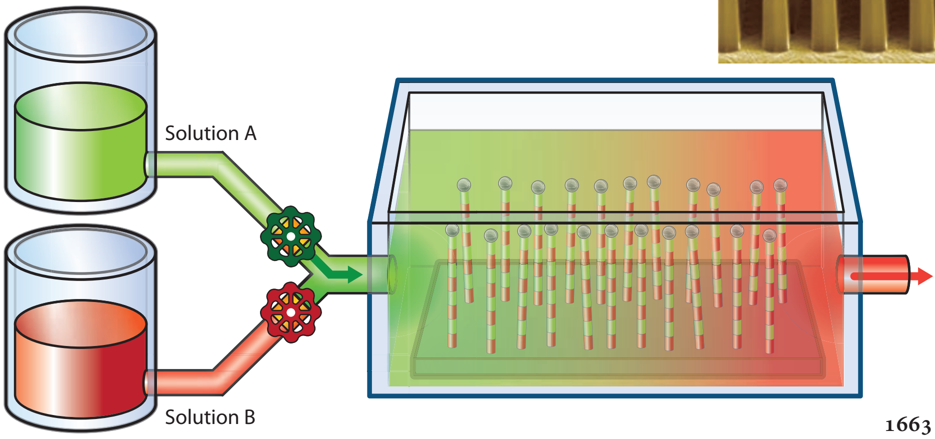
Jinkyoung Yoo and Jennifer Hollingsworth of Los Alamos examine nanowires grown by vapor-phase synthesis in the metal reaction chamber at left.

To obtain the necessary level of control, Hollingsworth decided on a microfluidic reactor platform, which recently came to fruition thanks to several postdoctoral researchers. Nick Smith (who has been promoted to Los Alamos research staff) started the effort, which was then perfected by postdoctoral fellow Rawiwan Laocharoensuk, with help from Kumar Palaniappan.

Microfluidics generally refers to the manipulation of fluids flowing in small-volume channels, typically less than a millimeter wide, as in ink-jet printing. In the case of the flow-SLS microfluidic reactor, a thin tube carries the semiconductor reactants (and some coordinating molecules called ligands) in a solvent into a resealable, computer chip-sized chamber. There, the solution flows over a substrate littered with liquid-metal catalyst droplets. The semiconducting material supersaturates the droplets and grows nanowires from the solid surface below them, just like vapor-phase synthesis, and the byproduct-containing solution flows out of the chamber.

Nanowire growth with flow-SLS isn't as rapid as in standard solution-based synthesis, but it provides for a number of reaction parameters that can be carefully dialed up or down





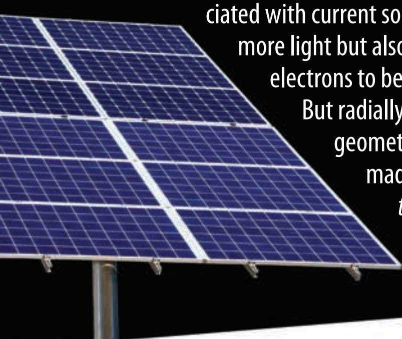
Heterostructured nanowires, in which wire segments made from different semiconducting materials are joined together, can be used in electronic components for a wide range of applications. (Below) In Hollingsworth's solution-based flow-SLS production method, axially heterostructured nanowires—with different semiconducting materials along the length of the wire—are made by alternating the solutions flowing into the reactor. (Right) Again using alternating reactants, but in the vapor phase, Yoo was also able to make radially heterostructured nanowires, in which the differing semiconductors are arranged concentrically like tree rings. Shown here are heterostructured silicon *p-n* junction nanowires (see main article) for use in solar cells.

BIG ENERGY from the littlest wires

Solar Cells

Silicon nanowire solar cells have the potential to achieve better light collection and lower production cost compared to existing silicon solar cells. Bulk, planar silicon cells reflect—and therefore waste—a substantial amount of the incident sunlight, but nanowire forests have been constructed in a way that scatters light from wire to wire, trapping it until it can be absorbed. And because of the gaps between the wires, nanowire solar cells can be produced with much less bulk, and even on less expensive substrates, than existing solar cells.

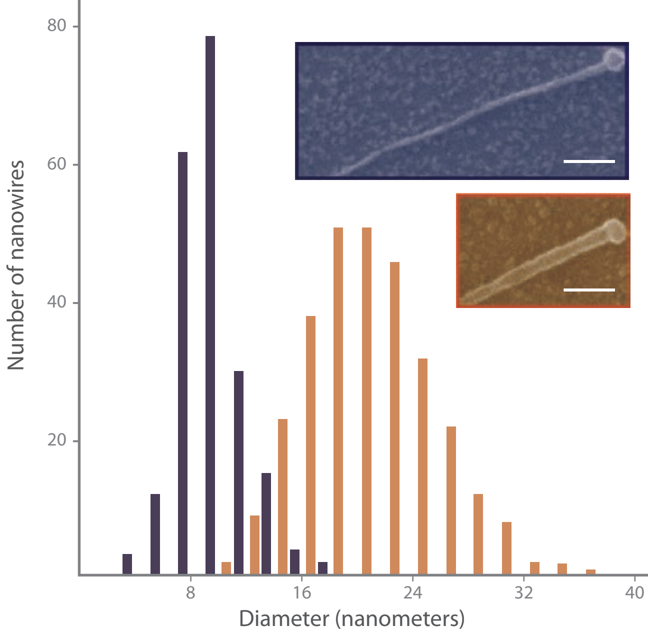
Los Alamos's Jennifer Hollingsworth and Jinkyoung Yoo both contribute to nanowire solar power research. Hollingsworth is working from solution-cast nanowires and relying on their ability to "sensitize" other semiconductors to solar energy. Yoo is constructing radially heterostructured nanowires (see main article) to help resolve a major trade-off associated with current solar cells: Thicker silicon layers absorb more light but also allow more time for solar-produced electrons to be lost in a process called recombination. But radially heterostructured nanowires have a geometric advantage because they can be made *longer* to absorb more sunlight, but *thinner* to reduce the time available for recombination.



Rechargeable batteries

Lithium-ion batteries are already used in phones, computers, electric cars, and just about everything else. Their storage capacity is limited by the amount of lithium that can be held in their anodes, which are currently made from carbon graphite. They could store 10 times more electrical charge (and last 10 times longer) if their anodes were made from silicon instead, but bulk silicon's advantage is also its undoing. Because it draws in so much lithium, its volume swells and contracts during charging and discharging, causing it to fracture. Over several charging cycles, damage accumulates and the storage capacity declines. However, the thin, extruded shape of silicon nanowires can accommodate the volume change without damage, allowing vastly greater storage capacity over many more charging cycles than existing lithium-ion batteries. Former Los Alamos researchers Tom Picraux and Jeong-Hyun Cho achieved several hundred charging cycles of reliable battery performance with many times the energy storage capacity of existing batteries just by optimizing the structural quality of bulk silicon. Yoo is working to raise their success to the next level with nanowire silicon.

With their flow-SLS protocol, Hollingsworth and her team were able to adjust the diameter of the nanowires they produced by varying the thickness of the bismuth film that breaks into catalyst droplets and the rate at which they flow reactants into the microfluidic reactor. Thinner nanowires resulted from thinner catalyst films and faster reactant flow rates. The histogram shows the range of nanowire thicknesses resulting from a relatively thin, 5-nanometer-thick bismuth film. Blue indicates nanowires obtained with a flow rate 10 times faster than that for orange. White lines in the inset micrographs are 100 nanometers long.

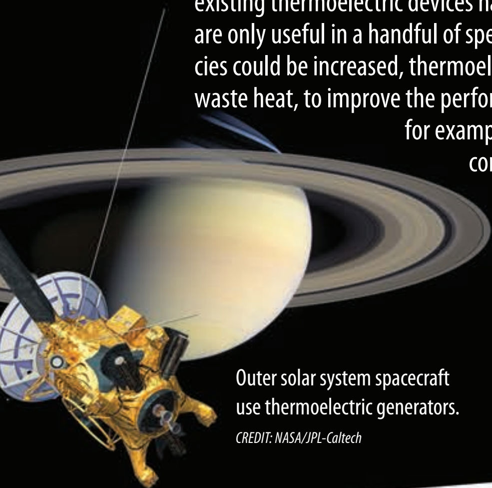


to improve the output. For example, by decreasing the size of the catalyst droplets, adjusting the reaction temperature, and increasing the flow rate, Hollingsworth's team was able to build single-crystal wires 5–8 nm in diameter—well within the useful quantum confinement regime for controlling the semiconductor energy gap. And by injecting an alternating sequence of two different semiconducting materials, they were able to make heterostructured nanowires, as needed for semiconductor electronics and other applications.

Once the flow-SLS process has completed, the wires can be harvested from the substrate and arranged as needed for whatever application is at hand. And because of their solubility, they can be delivered in industrially convenient ways, such as spray-on inks and dip-coatings. So far, solution-liquid-solid growth has produced nanowires more like spaghetti than a forest—but Hollingsworth says that with flow-SLS, a

Thermoelectric devices

When a circuit made from certain materials spans a temperature difference (one end of the circuit is hotter than the other), the thermoelectric effect causes an electrical current to flow. This effect is often exploited in temperature sensors and can be used for very specialized power production applications, such as generating electricity from the heat-producing plutonium cells that power long-range spacecraft. However, existing thermoelectric devices have very low efficiencies and therefore are only useful in a handful of specialty applications. If their efficiencies could be increased, thermoelectrics could generate electricity from waste heat, to improve the performance of a solar panel or a car engine, for example. Nanowires can deliver electrical conductivity without much thermal conductivity, helping to maintain the temperature difference. But very little temperature difference can exist across the tiny length of a nanowire, so Hollingsworth is researching different web-like networks of nanowires to increase the temperature difference they can sustain.



Outer solar system spacecraft use thermoelectric generators.

CREDIT: NASA/JPL-Caltech

Lighting and lasers

Light-emitting diodes, or LEDs, produce light at a much lower energy cost than incandescent and fluorescent sources, but they are expensive to manufacture and have limited emission colors. Here, Hollingsworth focuses on specialized nanocrystal quantum dots that she and her team developed with unique properties that make them particularly useful for light emission. They can serve as the active component in an LED (electrically stimulated to emit light) or perform color conversions from blue light to green, yellow, or red, much like rare-earth compounds do in fluorescent lights and white-emitting LEDs today.

"Unlike solar and battery applications, which are very cost-sensitive, LEDs and other high-efficiency lighting are already expensive anyway," Yoo says. "So even a somewhat costly nanoparticle LED has a good chance of succeeding in industry, as long as it's efficient and delivers the right kind of light."

forest is achievable, too; it's just a matter of properly matching the semiconductor nanowire with its substrate.

In essence, she and her team achieved creative control over the nanowire production process in a relatively inexpensive, versatile, solution-based alternative to vapor-phase synthesis. Their innovation may help usher in an era of bona fide nanowire commercialization. Yoo agrees that flow-SLS is a "really smart way" to make nanowires for various future applications, even though the vapor-phase approach he works on has a substantial head start in R&D.

Nanowired world

Just what kinds of technological breakthroughs would a production-scale nanowire industry bring about? Most people in the nanotech field would jump to computing, noting the potential quantum leap in transistor miniaturization that crossed heterostructured nanowires represent. Others would point to biomedical applications inspired by the availability of tiny sensors. But not surprisingly, at CINT, and within the DOE more broadly, the focus is largely on energy. And the nanowire-energy revolution is just getting started.

Nanowires are almost certainly capable of significantly boosting solar power efficiency and rechargeable battery life. They are also likely to enable much lower-cost lighting than is currently available. (That benefit alone would be worth the effort; lighting amounted to 12 percent of all U.S. electricity consumption in 2011, according to the Energy Information Administration.) Nanowires may even revolutionize thermoelectric devices, which could then be used to harvest electrical energy from any source of waste heat—and virtually all energy production processes, and many other industrial processes, produce wasted heat. Together, these energy-related nanowire applications could drastically reduce the economic and environmental costs of human energy use. (See "Big Energy from the Littlest Wires" above.) Such is the potential for energy advances that persistently entices Hollingsworth, Yoo, and perhaps everyone else in the nano-energy innovation business. It consumes their every thought—almost.

In her small, packed office at CINT, Hollingsworth changes gears. Instead of continuing to describe her flow-SLS research and its potential for solar or thermal energy harvesting, or her quantum dot lighting research, or any of the semiconductor and chemical-synthesis fundamentals that underlie it all—instead of that, she mentions something new. It's another nanoparticle application that she's pursuing: a new nanoparticle to someday simultaneously image and treat cancer by selectively generating both light and heat—to expose and then attack a tumor inside the body—for a controlled kill.

"You know," she says impassively, "instead of chemo."

LDRD

—*Craig Tyler*